

PLASMA NITRIDING OF A PRECIPITATION HARDENING STAINLESS STEEL TO IMPROVE EROSION AND CORROSION RESISTANCE¹

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Abstract

Precipitation hardening stainless steels are used as structural materials in the aircraft and the chemical industry because of their good combination of mechanical and corrosion properties. The aim of this work is to analyze the structural changes produced by plasma nitriding in the near surface of Thyroplast PH X Supra®, a PH stainless steel from ThyssenKrupp, and to study the effect of nitriding parameters in wear and corrosion resistance. Samples were first aged and then nitriding was carried out in an industrial facility at two temperatures, with two different nitrogen partial pressures in the gas mixture. After nitriding, samples were cut, polished, mounted in resin and etched with Vilella reagent to reveal the nitrided case. Nitrided structure was also analyzed with XRD. Erosion/Corrosion was tested against sea water and sand flux, and corrosion in a salt spray fog (ASTM B117). All nitrided samples presented high hardness. Samples nitrided at 390°C with different nitrogen partial pressure showed similar erosion resistance against water and sand flux. The erosion resistance of the nitrided samples at 500°C was the highest and XRD revealed nitrides. Corrosion resistance, on the contrary, was diminished; the samples suffered of general corrosion during the salt spray fog test.

Keywords: PH stainless steel; Plasma nitriding; Corrosion.

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1 INTRODUCTION

Plasma Surface Engineering gathers a group of different techniques oriented to modify a material surface. One of these techniques is plasma nitriding using a DC pulsed power supply. This is a plasma assisted thermochemical process, in which the work-piece acts as a cathode. The ion bombardment heats the workpiece, cleans the surface and provides active nitrogen. As a result, the hardness achieved on the surface is the highest and its value decreases with depth until the core hardness is reached. Ion nitriding has proved to be a suitable hardening process for stainless steels, improving wear resistance.^[1-4] Provided a good control of process parameters such as temperature and process time, corrosion resistance of austenitic stainless steels can be unaltered and even improved due to the formation of the so called "S" phase, which is a nitrogen supersaturated expanded austenitic phase.^[5,6] In the case of martensitic stainless steels, however, corrosion resistance is still an issue, because of their low chromium content and the formation of chromium carbides, during quench and tempering heat treatment, and chromium nitrides during nitriding.^[7,8] Precipitation hardening (PH) stainless steels could be better candidates than martensitic steels for plasma nitriding, because they do not need to go through the quenching and tempering treatment; they only need an aging treatment around 500°C to obtain their hardness and mechanical properties, which are based on the formation of fine precipitates. Besides, they have low carbon content and consequently chromium carbides precipitation could be reduced.

In the case of PH stainless steels there are published papers^[9-11] that present some promising results if a low temperature process (around 350°C-380°C) is applied. On the other hand, Estafandari and Dong^[12] obtained good corrosion results nitriding 17-4 PH at 500 °C and forming a dense layer of iron nitrides.

PH X SUPRA is a Cr-Ni alloy, a PH martensitic stainless steel with Cu and Nb additions. This steel is used for several applications that demand good wear and corrosion resistance. Its good corrosion resistance in acids and climatic conditions such as high humidity or sea air lies in the homogeneous microstructure with a minimum of carbides. These features make it especially useful for plastic moulds, chemicals process equipment, jet engine parts, air craft fitting and nuclear reactor among others.

In this work a study of wear and corrosion resistance of nitrided PH X Supra stainless steel is presented, comparing three different nitriding conditions, involving temperature and partial nitrogen pressure.

2 EXPERIMENTAL

Disc samples of Thyroplast PH-X Supra steel were sliced from a bar provided by Fortinox Thyssen Argentina, and fabricated by Deutsche Edelstahlwerke GmbH, Germany. Composition is the following: 0.05% C, 15% Cr, 4.5% Ni, 0.45% Mn, 0.25% Si, 3.5% Cu, a little content of Nb and Fe as balance. The samples were solution treated to be cut and machined, after that they were hardened prior to nitriding according to supplier recommendations, by means of an aging process at 495°C for 4 hours.

Nitriding was carried out for 10 hours in an industrial facility described elsewhere^[13] at two temperatures, 390°C and 500°C. The gas mixture used at 390°C was 25 % N₂ + 75 % H₂ (named condition 1) and 20 % N₂ + 80 % H₂ (condition 2) while at 500°C a mixture of 25 % N₂ + 75 % H₂ was used (condition 3). The

nitriding process were carried out in a DC pulsed discharge and was initiated with a sputtering stage. Sputtering and nitriding parameters are summarized in Table 1.

Table 1. Nitriding process parameters

| | |
|---|------------------------------|
| Sputtering Time | 3 hours |
| Sputtering gases | Ar, H ₂ , 50% 50% |
| Nitriding Time | 10 hours |
| Mean voltage | 700 V |
| Nitriding pressure | 650 Pa |
| Pulsed discharge t _{on} - t _{off} | 70 μs – 200 μs |

After heat treatment and nitriding, surface hardness of all samples was tested with a microhardness tester HV Shimadzu with a Vickers indenter and 50 g load. After the nitriding process, one sample of each group was cut, polished, mounted in resin and etched with Vilella reagent 60 seconds to reveal the nitrided case. The surface microstructure was also analyzed with XRD, using a Philips PW3710 diffractometer operated with Cu-K α radiation.

Erosion resistance was tested against sea water and sand flux during 24 hours at a temperature of 60 °C; the samples rotated in the slurry solution at a mean tangential velocity of 7 m/s. Samples were placed to have contact with the sand at normal incidence. Sand with AFS granulometry 50 was used, with a concentration 125 g/l. Sea water was simulated with a solution of 1% NaCl and 0.3% MgCl.

Salt fog spray tests were conducted in a self made chamber according to ASTM B117.^[14] The solution used for salt spray was 5% NaCl of ph 6.8 and the experiments were carried out at a temperature of 32°C, during 100 hours. Results were evaluated qualitatively, observing the presence of rust.

3 RESULTS

3.1 Microstructure and Hardness

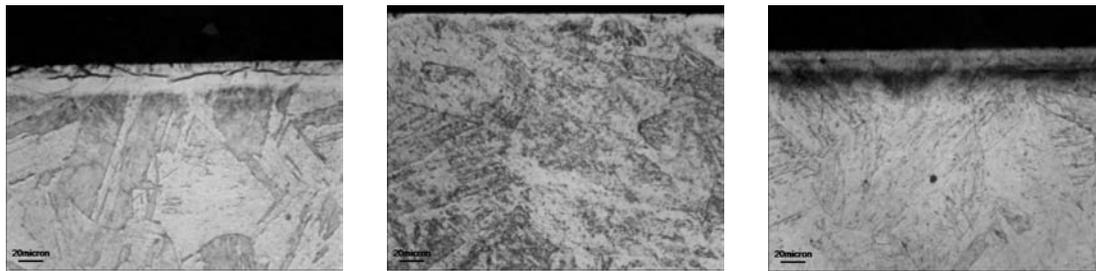
This material has achieved a hardness of (490 ± 10) HV after aging heat treatment. The first column of Table 2 shows that the surface hardness resulted very similar after the three nitriding conditions, indicating that a compact nitrided layer was formed. Figure 1 shows three micrographs with 400x magnification, where a white layer can be observed on the surface, below is the martensitic structure of the bulk.

Table 2. Hardness and microstructure characteristics of the different samples

| Condition | Hardness [HV50g] | Nitrided layer width | Dark layers |
|---------------|------------------|----------------------|-------------|
| Nitr. Cond. 1 | 1360 ± 10 | 24-25 μm | No |
| Nitr. Cond. 2 | 1330 ± 30 | 7-8 μm | No |
| Nitr. Cond. 3 | 1360 ± 30 | 13-14 μm | Yes |

It can be observed that in the first micrograph, which corresponds to a sample nitrided in Condition 1, that several cracks parallel to the surface were produced within the nitrided layer. On the contrary, sample nitrided in Condition 2, shows a

regular but narrower nitrided layer. Finally, the third micrograph which corresponds to the sample nitrided in Condition 3, 500°C, shows the thickest nitrided layer, not white but gray, indicating that it was sensitive to the Vilella etchant.



Cond. 1: 25% N₂ - 390 °C Cond. 2: 20% N₂ - 390 °C Cond. 3: 25% N₂ - 500 °C
Figure 1. 400x magnification micrographs of nitrided samples.

XRD analysis of the non nitrided sample shows the classic peaks of a martensite structure, called the α' phase and some little amount of retained austenite (γ), as it is presented in Figure 2a. The non nitrided diffractogram is depicted in black. After nitriding the austenite is transformed in nitrogen expanded austenite and which is called the γ_N phase. Besides, for nitrogen activities above a certain threshold value the transformation of b.c.t. (α'_N) to f.c.c. (γ_N) occurs, because of the stabilizing effect of nitrogen on austenite.^[10,15]

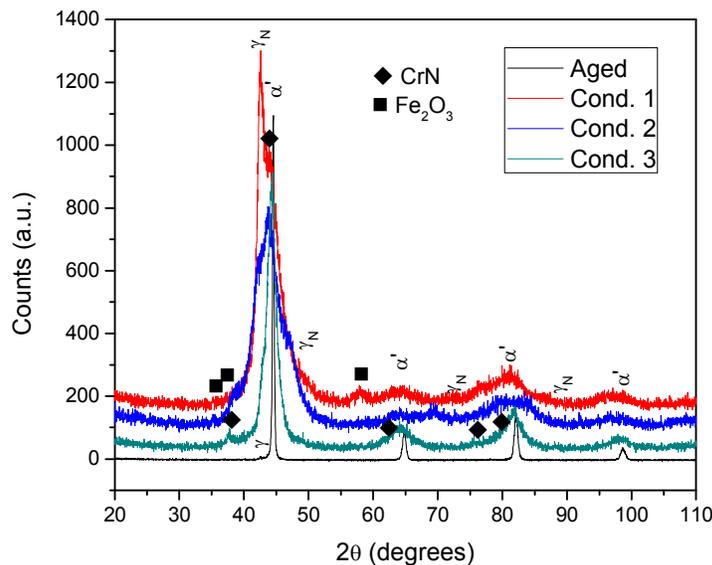


Figure 2a. Complete XRD spectrum of all samples.

The martensite peaks are shifted to lower angles showing a lattice expansion and they are also broader, showing that the nitriding process generates microstresses and defects. In Figure 2b, only the 35°-55° 2θ region is depicted to allow a better observation of the main peaks. Chromium nitrides (CrN) are only present in the sample nitrided in Condition 3 (500°C) and there's no sign of iron nitrides γ' or ϵ .

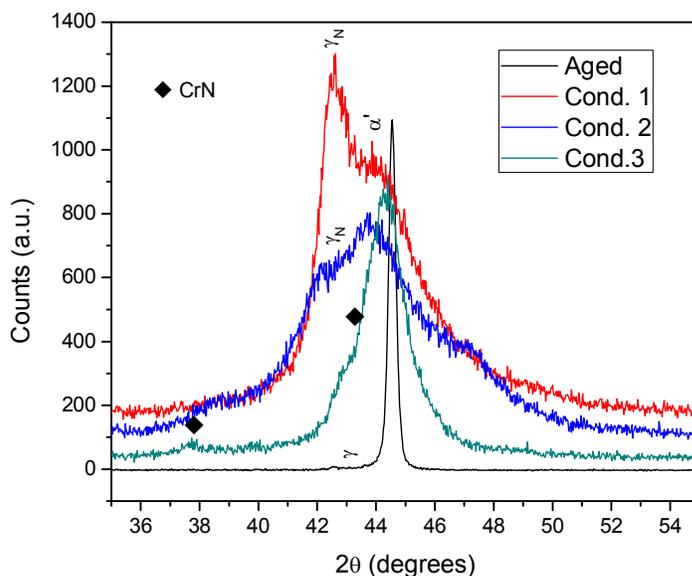


Figure 2b. XRD spectrum $35^\circ < 2\theta < 55^\circ$.

3.2 Erosion / Corrosion

Erosion / corrosion results of two samples of each condition were characterized by mass loss in relation to a control sample, which was the same material with the aging treatment but non nitrided. Results are presented in Table 3.

Table 3. Erosion/corrosion results: relative mass loss to non nitrided sample

| | Relative Δm_1 | Relative Δm_2 |
|---------------|-----------------------|-----------------------|
| Nitr. Cond. 1 | (204 ± 10) % | (282 ± 10) % |
| Nitr. Cond. 2 | (40 ± 1) % | (48 ± 1) % |
| Nitr. Cond. 3 | (100 ± 2) % | (123 ± 2) % |

The sample nitrided in condition 1 lost more than two times the mass which lost the control sample (non nitrided), from the volume loss it was calculated that these samples lost the whole nitrided layers. The sample nitrided in condition 3 had a similar erosion corrosion resistance than the control sample, but they also lost the nitrided layer. Only the samples nitrided in condition 2, even though the nitrided layer was thinner, had a better behavior in this test, showing less than half of mass loss than the non nitrided sample.

Photographs of the eroded surface are presented in Figure 3 with 50x magnification for each nitriding condition. The non nitrided sample was uniformly eroded and the micrograph is not presented. It can be observed in the micrograph of condition 1 that plastic deformation was much more severe than in the sample of condition 2. In the eroded sample nitrided in condition 3, a vertical crack can be observed in the middle of the surface, indicating that the nitrided layer underwent brittle fracture.

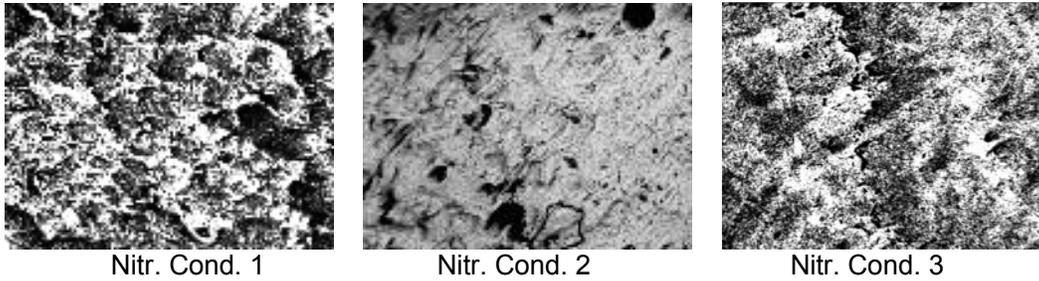


Figure 3. Eroded surfaces of nitrated samples.

3.3 Corrosion in Salt Spray Fog

After 100 hours exposure in the salt spray fog test, photographs of the exposed surfaces were taken, cleaned only with rinsing water. The non nitrated sample was clean with no sign of general or local corrosion. Pictures of nitrated samples are shown in Figure 4a, where it can be observed that samples of Condition 1 and 3 (25% N₂) suffered of severe general corrosion. Sample of Condition 2 (20% N₂) on the contrary, was not so damaged. All samples were then slightly grinded to remove corrosion products, and it was revealed that only sample of cond. 2 had an acceptable corrosion behavior with only a few pits in the border regions of the sample.

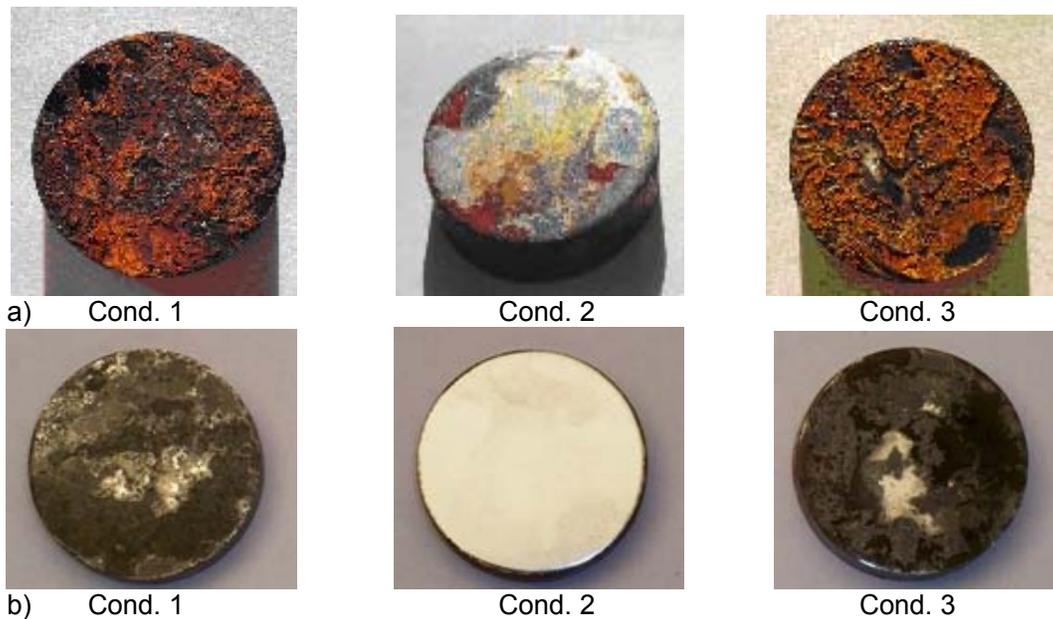


Figure 4. Surface aspect after salt spray fog test, without (up) and after (down) grinding.

4 DISCUSSION

It is clear from the results that nitriding can produce a detrimental effect not only in corrosion resistance in stainless steel but also in wear resistance, specifically erosion. Only samples nitride in condition 2, 390°C and 20% N₂ - 80 H₂ nitriding atmosphere, showed a good erosion resistance and an acceptable corrosion behavior. It was reported in many previous works on all sort of austenitic and martensitic stainless steels that nitriding always produces a hardened surface layer

with a better wear resistance and also if the process was performed at a temperature around or lower than 400°C the corrosion resistance can be sustained.^[3,5,7,9] It is also known that harder means also brittle, and that is an inconvenience for certain types of wear mechanisms, such as erosion with hard particles,^[16] as it was the case observed in samples nitrided in condition 3 in the experiment described previously. The surface hardness was the highest, the nitrided layer, the thickest, but it collapsed during the erosion test. Also within this hard layer chromium nitrides precipitated as it was indicated in the XRD analysis and the corrosion resistance diminished, which it could be demonstrated not only in the salt spray fog test but also in the micrograph, where the dark layers formed after etching with Vilella reactant.

A work was published by Esfandiari and Dong^[12] where a PH steel was nitrided 10 and 30 hours at 500°C and a good corrosion behavior resulted, coming from the formation of a compound layer of Cr and Fe nitrides. In the experiment described here, XRD demonstrated that in this steel, such compact compound layer was not formed, the nitrided layer consisted in expanded austenite, nitrogenated martensite and some CrN precipitates. The steel used here is not exactly the same as the one mentioned in the above reference and other nitriding conditions such as current density and voltage were not assessed, being these factors the probable cause of the difference between the results.

In this work it was also demonstrated that it is important not only the high temperature but the amount of nitrogen in the nitriding atmosphere, because the samples nitrided in condition 1 and 2, both at low temperature (390°C), showed totally different behaviors in the erosion corrosion test so as in the salt spray fog test. The sample nitrided in condition 1, with 25% N₂ partial pressure, showed cracks parallel to the surface and the nitrided layer was easily broken and removed during the erosion test. In the condition 2, only by means of reducing the nitrogen partial pressure from 25 % to 20 %, these cracks were avoided, the nitrided layer was three times thinner but hardness was sustained and showed a good wear resistance in the erosion/corrosion test where the mass loss indicated that the nitrided layer was not totally removed. From the observation of the surface it can be concluded that this layer suffered plastic deformation and not brittle fracture.

The samples nitrided in this condition were, on the other side, the only ones which showed acceptable corrosion resistance in the saline environment, general corrosion did not occurred (as in the other samples) because after removing corrosion products only a few pits of localized corrosion were observed, showing that the classic passive behavior of the stainless steel was somehow retained.

5 CONCLUSION

When nitriding precipitation hardening stainless steels of the type 15-5 PH like the one used in this study, PH X Supra from ThyssenKrupp, lower temperatures are recommended, namely 390°C allows to form a 10 microns layers with no compound precipitation regions (dark regions). If nitrogen partial pressure remains in 20% the nitrided layer is not brittle, has no cracks and a good erosion resistance can be achieved.

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